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and Solid State Studies"

by

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## MIXED VALENCE IN CONJUGATED ANION RADICALS. SOLUTION AND SOLID STATE STUDIES

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### ABSTRACT

Electron localization in anion radicals of aromatic compounds built with two electrophores was studied using Vis, NIR, IR and ESR spectroscopy and electrochemistry. N,N',-Bis(2,5-di-tert-butylphenyl)-2,3,6,7-anthracene-dicarboximide anion radical has the odd electron mainly localized on the anthracene bridge. This contrasts with its diquinone analog, 1,4,8,11-pentacenetetrone, which has the odd electron localized on one quinone at a time. The anion radical of the tetrakis-(N-cyanoimine) derivative of 5,7,12,14-pentacenetetrone ( $3^-$ ) is delocalized. The solid state conductivity of the salts  $M^+$ ,  $3^-$  ranges from  $10^{-4}$  S  $\text{cm}^{-1}$  for  $M=\text{Bu}_4\text{N}$  to 0.4 S  $\text{cm}^{-1}$  for  $M=\text{Na}$ .

### INTRODUCTION

An understanding of the properties of synthetic metals can be approached by dissecting the problem into single molecule properties and intermolecular interactions. According to this approach, model compounds are prepared which, when studied in solution, mimic the intramolecular properties of the synthetic metal. The model compound is then incorporated into a solid in order to compare its properties with that of the synthetic metal of interest. This approach is not so easy to implement because model compounds of synthetic metals must have some unusual characteristics. Typically they must have long delocalization lengths and have some mixed valence character. For example, a neutral polyene is not likely to be a good model for polyacetylene, which only conducts electricity when it is partially oxidized or reduced. As another example, it has been shown that the properties of radical-ion  $\pi$  dimers are quite different from the delocalized  $\pi$  stacks of radical-ions in conducting organic salts. In contrast a partially oxidized oligothiophene<sup>1</sup> or an oxidized oligoaniline<sup>2</sup> should be

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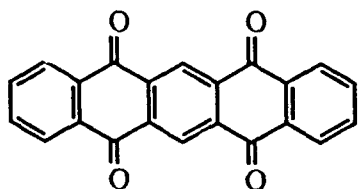


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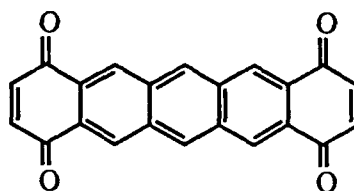
good models for their respective conducting polymers. Because these model ionic species are often not very stable, this dissection philosophy has been implemented in only a few cases.<sup>1-3</sup>

In the present study we are using model anion radicals to probe the concept of electron localization. This concept is central to understanding the electrical and magnetic properties of synthetic metals. In the intramolecular sense localization means that the conduction electron is localized at some atom or group along a conjugated  $\pi$  system, so as model compounds we are investigating functionalized aromatic anion radicals in which the odd electron can be localized on electron accepting groups like quinones or imides. These relatively rigid aromatic compounds are of special interest because they do not have the possibility of localization through rotation about single bonds as in polyene ions. Our previous studies have revealed that certain diquinone anion radicals like **1**<sup>-</sup> can be considered delocalized,<sup>4</sup> while others in which the two quinones are separated by two or more rings like **2**<sup>-</sup> have spectroscopic properties which suggest localization.<sup>5</sup> Thus, the odd electron is thought to be localized on one quinone or the other, jumping back and forth rapidly at room temperature. To our knowledge, this constitutes the only example of this phenomenon in a planar, aromatic  $\pi$  system. However, some similar phenomena have been reported for the anion radicals of certain dinitro compounds<sup>6</sup> and a bis-indanone<sup>7</sup>, and the cation radical of an N,N-dialkoxyurea.<sup>8</sup>

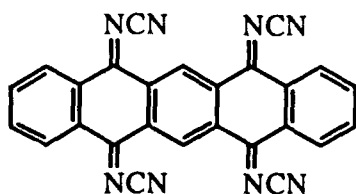
It was our goal in this phase of the investigation to explore functional groups similar to quinones and to vary the aromatic moiety between the electron accepting groups. We report here a comparison of the properties of four radical anions (**1**<sup>-</sup>-**4**<sup>-</sup>). We describe the synthesis, the cyclic voltammetry, the Vis, near infrared (NIR), and IR spectra of solutions, as well as solid state conductivity and IR data. The solid anion radical salts of **3**<sup>-</sup>, like those of **1**<sup>-</sup>,<sup>9</sup> are unusual in that they exhibit high conductivity even though charge transfer to the counter cation is complete.



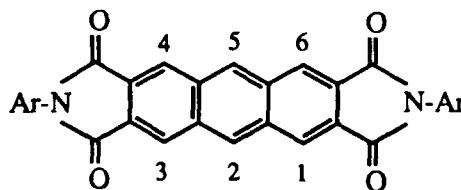
**1**



**2**



**3**



**4** Ar = 2,5-di-(tert-butyl)phenyl

## RESULTS AND DISCUSSION

### Diquinone Tetraimine Anion ( $3^-$ ) Compared to Diquinone Anion ( $1^-$ )

It has been shown that the odd electron in radical anion  $1^-$  is delocalized<sup>4</sup> so it was of interest to prepare an analog with functional groups that are better electron acceptors than the quinones. Such an anion radical might localize the electron on one end or the other. To that end we prepared the anion radical  $3^-$ , which has N-cyanoimine groups replacing the quinone carbonyls. The work of Hunig and Aumuller,<sup>10</sup> and others,<sup>11</sup> has established that these derivatives are easier to reduce than quinones, suggesting that the N-cyanoimine is a better electron acceptor than a carbonyl.

As reported in a preliminary communication,<sup>12</sup> compound **3** was prepared by the reaction of diquinone **1** with bis(trimethylsilyl)-carbodiimide in methylene chloride with titanium tetrachloride. After purification and characterization it was studied electrochemically. Cyclic voltammetry using degassed 0.1 M  $\text{Bu}_4\text{NBF}_4$  in DMF solvent gave four one-electron couples. The first two couples have anodic-cathodic peaks separated by 60 mV and the peak potentials are independent of sweep rate over the range 20-1000  $\text{mV s}^{-1}$ . The third and fourth couples are quasi-reversible. The apparent  $E^\circ$  values derived from these voltammograms are 0.10, -0.15, -0.91 and -1.11 V (SCE). The first reduction takes place at extremely positive potentials. Compound **1**, for comparison, reduces at -0.42 V.<sup>4</sup> While compound **1** shows a separation between first and second reductions of 500 mV, **3** has only 250 mV between the first and second peaks. After a separation of 760 mV between the second and third peaks, the third and fourth are spaced close together (200 mV) like the first two. This is notable because it is well known that closely spaced redox potentials are a common property of compounds which give Type II mixed valence ions and conducting solids.

Coulometric reduction of **3** was performed using a carbon sponge cathode in DMF,  $\text{Bu}_4\text{NBF}_4$ . The cell was divided to prevent reoxidation of the electrogenerated anions at the anode. By controlling the number of coulombs passed it was possible to produce the mono-, di-, tri- and tetra-anions sequentially. The success of this endeavor was demonstrated by IR spectroscopy. Thus, after passage of 1,2,3 and 4 Faradays/mole the cyano stretch showed shifts to lower frequency as more electrons were introduced. This is expected since the electrons go into antibonding orbitals and weaken the cyano bonds. Proceeding from neutral to tetraanion the IR frequencies were 2169, 2123, 2110, 2083 and 2078  $\text{cm}^{-1}$ .

Previous studies in this laboratory have established that certain diquinone anion radicals like  $1^-$  absorb at very long wavelength in the NIR. Indeed we have been interested in developing such compounds as NIR dyes.<sup>12</sup> In this case the coulometrically produced  $3^-$  showed an intense band with a maximum at 1520 nm ( $\epsilon=15,000$ ). This band shows vibrational structure with an apparent splitting of 1300

$\text{cm}^{-1}$ . This is quite similar to the wavelength (1335 nm) and splitting ( $1360\text{ cm}^{-1}$ ) found for  $1^-$ .<sup>4</sup> Also similar is the lack of solvent dependence of the spectrum. In dichlorobenzene solvent,  $3^-$  absorbs at 1530 nm, only  $40\text{ cm}^{-1}$  away from the peak maximum in DMF. These observations rule out a charge transfer absorption and strongly suggest a  $\pi^*-\pi^*$  transition, as has been well documented for  $1^-$  and its analogs.<sup>4</sup>

Preparative scale, coulometric reduction in DMF led to solutions from which were isolated the  $3^-$  salts listed in Table 1. These salts are all quite stable in the air. When redissolved in DMF they gave quantitatively identical Vis NIR spectra. In wet DMF  $3^-$  hydrolyzes over several days, while in the presence of  $\text{BF}_4^-$  the hydrolysis occurs over several hours. NIR spectra of the salts taken as NaCl or KCl pellets were different from the solution spectra. They showed a broad band near 1200 nm and a very broad band beyond 1500 nm which extended into the IR region. It is proposed based on many literature analogies<sup>13</sup> that this is a charge transfer band most likely arising from stacks of radical anions in the solid. In the case of  $1^- \text{Me}_4\text{N}^+$  an X-ray crystal structure determination established the validity of this structural analysis.<sup>9</sup> Examination of the tail of the NIR band in the IR shows that  $3^- \text{Na}^+$  absorbs at longer wavelength than the potassium salt, which is at longer wavelength than the tetrabutylammonium salt. An additionally interesting aspect of these IR spectra are the Fano bands, which are especially prominent in the spectrum of the potassium salt at  $2150$  and  $1600\text{ cm}^{-1}$ . The "negative" band at  $2150\text{ cm}^{-1}$  is ascribed to the coupling of an IR inactive cyano stretch with the active electronic transition.<sup>14</sup> This coupling produces a "hole" in the NIR band. These observations are quite consistent with the proposition that the longest wavelength NIR band comes from charge transfer.

Based upon the conductivity of  $1^-$  salts, the electrochemical and IR results, it was expected that the salts of  $3^-$  would be conductors. Pressed pellet samples of these polycrystalline samples were examined using the four point probe method. Room temperature conductivities (Table 1) ranged from  $10^{-4}$  to  $4 \times 10^{-1}\text{ S cm}^{-1}$ . The smaller counter cations gave higher values than the larger ones, with  $\text{Bu}_4\text{N}^+$  giving the smallest value. The relative values are consistent with the shift in the NIR charge transfer band to longer wavelength for the better conductor. Similar values and a similar sequence was reported for (air unstable) salts of  $1^-$ .<sup>9</sup> The trend might be understood by closer packing of the anion radicals for smaller counter cations.

It is unusual to observe such high conductivities for simple radical anion salts, in which the stacks are fully reduced. Usually it is necessary to prepare a charge transfer complex or make a mixed salt in order to raise the conductivity. It has been proposed<sup>9</sup> that these salts are different because they have the possibility of mixed valence for each anion along a stack without partial charge transfer to the counter ion. Not unexpectedly it did prove possible to prepare a charge transfer salt,  $3^- \text{TTF}$  by

grinding the two components together. After purification, this salt showed a conductivity of  $6 \text{ S cm}^{-1}$ .

Using  $3\text{-Bu}_4\text{N}^+$  it was possible to prepare single crystal material. The deep purple crystals were unfortunately too thin to give good single crystal diffraction data. It

Table 1. Conductivity Data For Salts of  $3^-$

<u>Cation</u>	<u>Conductivity (<math>\text{S cm}^{-1}</math>)</u>
Li <sup>a</sup>	$3 \times 10^{-1}$
Na	$4 \times 10^{-1}$
K	$5 \times 10^{-2}$
Me <sub>4</sub> N	$1 \times 10^{-2}$
Bu <sub>4</sub> N	$1 \times 10^{-4}$

a. Conductivities as high as  $4 \text{ S cm}^{-1}$  were obtained, but not reproducibly.

was shown, however, that the space group is  $P2_1/n$ . The unit cell holds four anions and has dimensions:  $a=17.0$ ,  $b=8.7$ ,  $c=25.4$ ,  $\beta=108^\circ$  and  $V=3566 \text{ \AA}^3$ .

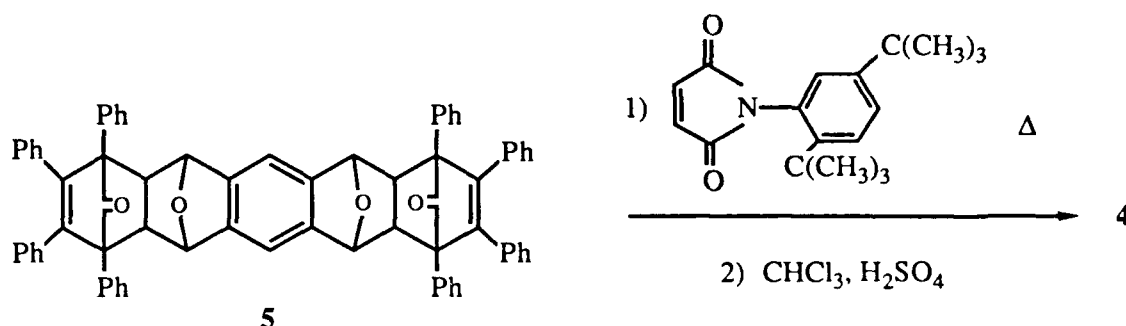
It is concluded from the NIR data that anion radical  $3^-$  is similar in structure to that of  $1^-$  with a delocalized ground state. On the other hand the close separation of electrochemical reduction peaks for **3** makes the possibility of Type II mixed valence behavior possible. It is known that the cross-over from Type III to Type II is in certain cases dependent on environment and we plan to investigate this possibility further.

#### **Diimide $4^-$ Compared to Diquinone $2^-$**

The spectra of  $2^-$  provided unexpected evidence for a difference in the electronic structure of this ion compared to that of  $1^-$ .<sup>5</sup> Based upon ab initio molecular orbital calculations it was proposed that this resulted from electronic localization. The calculations demonstrated that a localized electronic structure was lower in energy than the "normal" delocalized one, and that the ion was very polarizable so that small perturbations of the medium or nuclear positions would accentuate the localization. Here, we have explored the possibility that diimide  $4^-$  might localize like diquinone  $2^-$ . It was recognized that an imide was not as good an electron acceptor as a quinone and therefore the use of a diimide appeared to be a good choice to explore the cross over between localization and delocalization. In addition we were interested in employing the imide linkage to build larger aggregates, i.e. oligoimides.<sup>15</sup>

Compound **4** was prepared most efficaciously<sup>16</sup> using 1,2,4,5-tetrabromobenzene as a bis benzyne precursor, which reacted with furan and then in a second Diels-Alder

reaction with tetraphenylcyclopentadiene to give 5. This adduct was then reacted with N-(2,5-di-*tert*-butylphenyl) maleimide and dehydrated with sulfuric acid in chloroform. The product 4 was obtained in 83% yield and identified spectroscopically.<sup>16</sup> It had limited solubility, but it was more soluble than the 4-(*tert*-butylphenyl) derivative. We attribute this trend to the steric bulk of the butyl groups which make crystal packing more difficult.



Using cyclic voltammetry under the conditions cited above the reduction of 4 was explored. Two reversible couples were observed (60 mV separation of anodic and cathodic peaks) as well as some irreversible processes at more negative potentials. The  $E^0$  values for the reversible reactions were -1.07 and -1.53 V (SCE). This can be compared to the first two  $E^0$  values for 2 which are -0.72 and -0.84 V.<sup>5</sup> Clearly the diimide reduces much more difficultly than the diquinone. This arises because the imide group is not as a good electron acceptor as a quinone. The quinone double bond has an empty  $\pi^*$  orbital that can help to delocalize the odd electron, but the imide nitrogen has only the filled p orbital which cannot.<sup>16</sup>

Importantly the second  $E^0$  for 4 is nearly 500 mV more negative than the first, while the diquinone 2 adds a second electron only 120 mV beyond the first. Thus, cyclic voltammetry does not lead to the expectation that mixed valence is important for 4<sup>-</sup>.

The rather negative reduction potential of 4 signalled the possible instability of the ions. In fact, coulometric reduction of 4 gave solutions of the anion radical which were usually contaminated with some neutral. For this reason we turned to in situ NIR spectroelectrochemistry using a thin layer cell.<sup>17</sup> This device allowed a spectrum of the anion radical to be recorded every ten seconds. Over a period of two minutes the spectrum of the ion built up, there were appropriate isosbestic points, and reoxidation regenerated the spectrum of the neutral. The anion radical spectrum had peaks at 784 nm (log  $\epsilon$  4.34), 585 sh (4.10), 548(4.27), 485(4.66), and 453(4.39). There was no absorption with  $\epsilon$  greater than 1000 at wavelengths greater than 1000 nm. The spectrum does not resemble that broad (600-2400 nm) featureless spectrum found for 2<sup>-</sup>. Instead it is found in the region and resembles the complexity of the spectrum of

anthracene anion radical,<sup>18</sup> which has maxima at low temperature, matrix isolated 720 nm ( $\log \epsilon = 4.19$ ), 397(3.73), 368(4.61) and 333(4.51).

The structure of  $4^-$  was also investigated using ESR spectroscopy. The anion radical was electrogenerated in the ESR cavity using 0.1 M  $\text{Bu}_4\text{N BF}_4$  in DMF. Reoxidation led to loss of the signal and based upon the results cited above we feel confident that the spectrum (Fig 1) arises from  $4^-$ . The spectrum was successfully simulated using  $a_{\text{H}}(2\text{H})=5.50$ ,  $a_{\text{H}}(4\text{H})=3.90$ ,  $a_{\text{N}}(2\text{N})=0.98$  G. The larger proton coupling was assigned to the protons on positions 2,5 (see structural formula) by comparison with the spectrum of a derivative of  $4^-$ , which had methoxy groups attached at positions 2 and 5. The spectrum of the derivative anion radical lacked the 5.50G splitting, but showed  $a_{\text{H}}(4\text{H})=3.40$  and  $a_{\text{N}}(2\text{N})=0.75$  G as expected. This analysis demonstrates that the odd electron on  $4^-$  is not localized on one end of the molecule on the time scale of ESR. Indeed, the spectrum did not change on cooling to  $-60^\circ\text{C}$ . The large coupling constants for the anthracene bridge hydrogens suggest that the electron spends a lot of time on the bridge. For comparison, the 9,10 hydrogens of anthracene anion radical have  $a_{\text{H}}=5.4$  G. This is compatible with the appearance of the Vis spectrum and reinforces the proposal that the odd-electron is in a  $\pi^*$  orbital like that of anthracene anion radical.

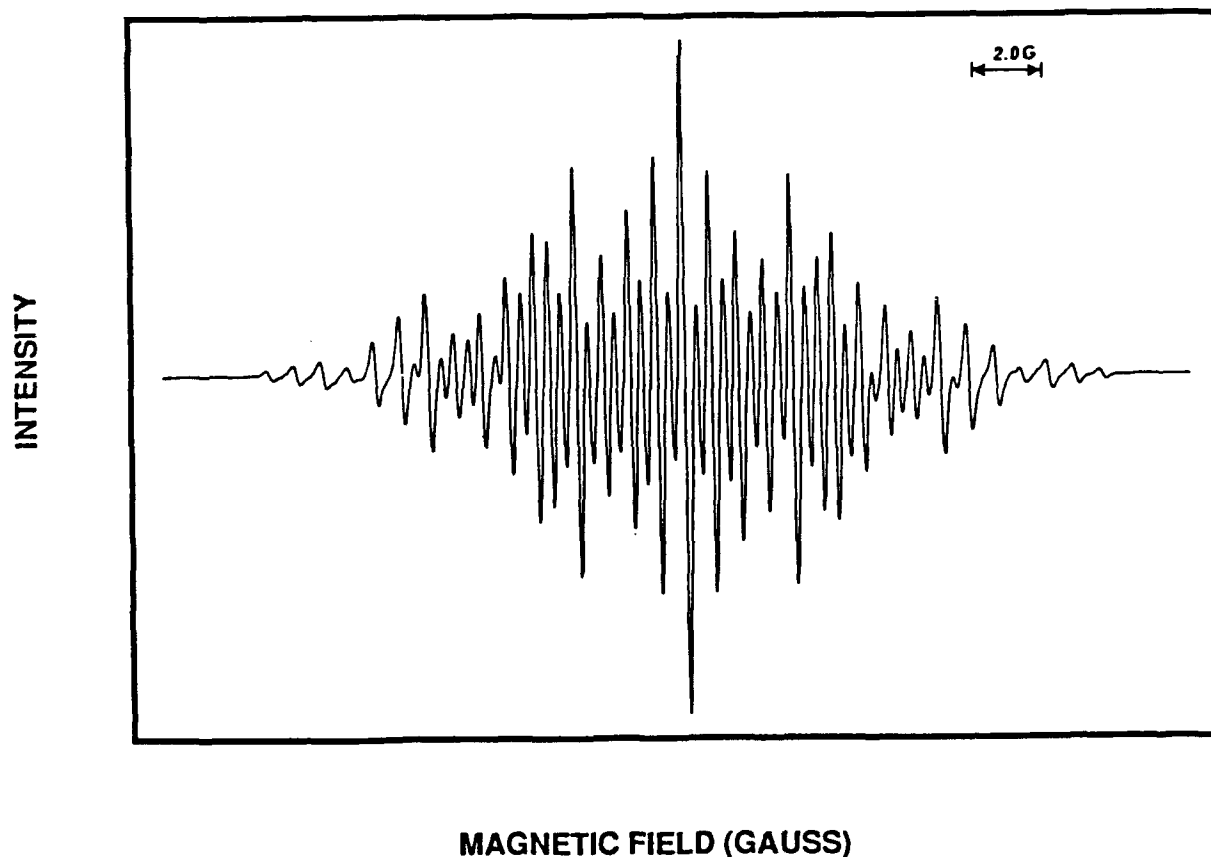


Figure 1. ESR spectrum of  $4^-$ .



There is concern, however, about our understanding of the electronic structure of  $4^-$ . We have established that Huckel M.O. calculations give reasonable estimates of the hyperfine coupling constants and long wavelength absorption maxima of a number of quinone and imide anion radicals (not including  $3^-$ ). There is not a good fit of experimental and calculated data for  $4^-$ . More specifically, a plot of experimental Vis-NIR transition energies vs. the SOMO-LUMO energy difference is linear for some 12 compounds,<sup>19</sup> but the point for  $4^-$  falls off of the line. The predicted wavelength from the calculation is about 2000 nm. For ESR, the Huckel electron densities used with the McConnell equation give  $a_H$  values that are usually within 0.3 G of the observed values for non-nodal positions. For example, the calculations give satisfactory agreement with the experimental  $a_H$  values for anthracene anion radical. The predictions for  $4^-$  are nodes at positions 2 and 5, and for the four equivalent hydrogens numbered 1,3,4,6  $a_H = 0.7$  G. This value is not close to the observed  $a_H$  of 3.90 G. In addition the 5.50 G coupling constant for the two hydrogens on the center ring is much too large for hydrogens attached to nodal carbons.

If  $4^-$  does not resemble  $3^-$  which has electrons localized on the ends of the molecule and does not conform to expectations for a delocalized molecule, what is its structure? Our suggestion is that  $4^-$  localizes the odd electron, but in the center of the molecule, not the ends. Considered in terms of the geometry changes which must accompany reduction it is suggested that for diquinone  $3^-$  the odd electron goes on to one quinone or the other, stretching its carbonyl bond lengths, but leaving the bridge bonds on average like those in the neutral. In contrast the diimide adds the odd electron in the center of the molecule, leaving the imide groups with bond lengths similar to those of the neutral. It is our immediate concern to test this hypothesis using appropriate M.O calculations on ion  $4^-$ .

## EXPERIMENTAL

### General

IR spectra were obtained as either KBr or NaCl pressed pellets or as a DMF solution in a CaF cell on a Perkin-Elmer 1600 FTIR instrument.  $^1\text{H}$  NMR spectra were obtained on an IBM AC 200 instrument in  $\text{CDCl}_3$  solution, with trifluoroacetic acid added to aid the solubility. Chemical shifts are in ppm downfield from TMS as referenced by the H impurity of  $\text{CDCl}_3$  at 7.25 ppm. UV-VIS spectra were obtained on a Shimadzu UV 160 spectrometer. NIR spectra were obtained on a Cary 17-D equipped with an IBM person computer for background subtraction and data storage. 1 cm and 0.1 cm pathlength quartz cuvettes (Helma) were used for UV-VIS and NIR solution studies. The radical anion salts were studied in the NIR as KBr or NaCl pressed pellets. Powder conductivities were measured on an Alessi 4 point probe

with a 44/1S head. Each pellet was measured in a minimum of 3 places, the variation typically being 20%.

Cyclic voltammetry was performed using a BAS-100 electrochemical analyzer. Bulk electrolyses were performed with a Princeton Applied Research (PAR) model 173 Potentiostat/Galvanostat equipped with a built in PAR 197 coulometer. Electrolytic preparations were performed both galvanostatically and potentiostatically giving similar results.

ESR spectra were recorded on a Bruker ESP 300 instrument using an in situ spectroelectrochemical quartz cell attached to a PAR potentiostat. The working and counter electrodes were Pt wires and the reference electrode was a Ag wire.

### Materials

Pentacenediquinone (**1**) was obtained by the method of Mills and Mills.<sup>20</sup> Trimethylsilyl carbodiimide was made by the method of Richter and co-workers.<sup>21</sup>  $\text{CH}_2\text{Cl}_2$  was distilled from  $\text{P}_2\text{O}_5$  prior to use. Dimethyl formamide (Mallinckrodt) was stored over activated AW-500 molecular sieves and passed through a column of activated alumina prior to use.

**Diquinone tetraimide 3.** 75 ml 1.0 M  $\text{TiCl}_4/\text{CHCl}_3$  is added to a mixture of 2.5 g **1** in 125 ml  $\text{CH}_2\text{Cl}_2$  under anhydrous conditions. The yellow solution slowly turns dark red after rapid dropwise addition of 20 ml bis-(trimethylsilyl)carbodiimide. The reaction mixture is refluxed for 16 hrs and cooled in an ice bath. After quenching with 300 ml cold  $\text{H}_2\text{O}$ , the yellow organic layer is carefully separated. The remaining emulsion is extracted with several small portions of  $\text{CH}_2\text{Cl}_2$ . The combined organic layers are then washed once again with water. After drying over  $\text{Na}_2\text{SO}_4$  the solvent is concentrated to 25 ml and the product is precipitated with petroleum ether. The crude yellow solid (1.8 g (56%)) is recrystallized from o-dichlorobenzene. IR: 2170, 1606, 1576, 1323, 1285  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR: 9.76(broad) 2H; 9.05(broad) 4H; 8.13(m) 4H. UV-VIS log  $\epsilon$  ): 287 nm (4.46), 345 nm (4.25).

**TBA<sup>+</sup> 3<sup>-</sup>.** **3** (0.1 g) was reduced in a two compartment cell containing 100 ml DMF, 0.1 M  $\text{Bu}_4\text{NBF}_4$ , with a reticulated carbon cathode and a carbon rod anode. After filtration to remove carbon particles, the salt was precipitated with diethyl ether. After 1 hr the salt was vacuum filtered. After several weeks the filtrate formed small plates from which the crystal data was obtained. The purple solid was purified by recrystallization from DMF. IR 2118  $\text{cm}^{-1}$ .

**Na<sup>+</sup> 3<sup>-</sup> and K<sup>+</sup> 3<sup>-</sup>.** **3** (0.1g) was reduced in a two compartment cell containing 100 ml DMF, 0.1 M  $\text{NaClO}_4$  or  $\text{KClO}_4$  using Pt electrodes. The solid was vacuum filtered and washed with DMF. IR: Na<sup>+</sup> 2131  $\text{cm}^{-1}$ , K<sup>+</sup> 2129  $\text{cm}^{-1}$ .

**TMA<sup>+</sup> 3<sup>-</sup>.** 0.050 g **3** was reduced in a 2 compartment cell containing 150 ml of a 50/50 mixture acetonitrile/ethanol (0.1 M  $\text{Me}_4\text{NI}$ ) using a Pt cathode and a carbon anode. The precipitate was filtered and washed with hot ethanol. IR: 2123  $\text{cm}^{-1}$ .

**Li<sup>+</sup> 3<sup>-</sup>.** 0.050 g **3** was reduced in a 2 compartment cell containing 150 ml acetonitrile (0.4 M LiI) using a Pt cathode and a carbon anode. The precipitate was filtered and washed with acetonitrile. IR: 2129 cm<sup>-1</sup>.

**TTF 3** Equimolar amounts of TTF (orange) and **3** (yellow) were ground together as solids with a mortar and pestle. The resulting black solid was recrystallized from DMF. IR: 2131 cm<sup>-1</sup>.

### Acknowledgement

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